

# Molecular Engineering and Photostability of Laser Dyes within Sol-Gel Hosts

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## ABSTRACT

The use of a solid-state dye laser for commercial applications has been limited largely by the poor photostability of the gain medium. Techniques are examined to improve the photostability of Coumarin and Pyrromethene-BF<sub>2</sub> 567 (PM-567) laser dyes within xerogel and Polyceram hosts synthesized by sol-gel processing. The photochemical mechanisms by which laser dyes degrade are discussed and determined specifically for PM-567. PM-567 was determined to degrade both by photo-oxidation and acid degradation. Techniques for improving photostability are described from a molecular engineering perspective. These techniques include: covalently attaching the laser dye to the host; controlling the chemical environment of the dye; increasing dye caging by increasing the SiO<sub>2</sub> content; removing porosity from the host; and incorporating additives such as hindered amine light stabilizers to minimize photodegradation.

**Keywords:** Pyrromethene-BF<sub>2</sub> 567, Solid-State Dye Laser, Sol-Gel, Polycerams, Photostability, Antioxidants, Porosity, Polydimethylsiloxane

## 1. INTRODUCTION

Lasing can take place in a variety of media, including solids, liquids, gases, and even plasmas. Liquid dye lasers are important because of their large wavelength tunability in the visible, low threshold powers, and pump source flexibility. Many families of lasing dyes exist such as Coumarins, Rhodamines, and Pyrromethenes. Most commercial lasing dyes are dissolved at low concentrations of 10<sup>-3</sup> to 10<sup>-4</sup> M in solvents (alcohols, H<sub>2</sub>O or ethylene glycol). Flow of the dye/solvent mixture through the resonator chamber is required to maintain photostability. This allows the dye molecules to move in and out of the pump beam within the resonator, giving the excited dye molecules time to return to ground state and minimizing dye degradation.

In the last several decades there has been much interest in developing a solid-state dye laser. The dye/solvent laser system requires fluid pumping devices, and therefore a solid-state medium would be a good alternative. A solid-state gain medium would avoid problems associated with dye/solvent systems, such as convection, evaporation, flow fluctuations, solvent poisoning, and dye poisoning<sup>1</sup>, and would provide ease of use and replacement, along with expanded applications as slab waveguide lasers, tunable fiber-optic lasers, and solid-state dye laser rods. Dye/host interactions could also enhance control of the fluorescence spectra, improve the quantum efficiency of fluorescence, and even improve photostability.

A tunable solid-state laser would have numerous applications in medicine. Currently, liquid dye lasers have potential use in dermatology for the removal of vascular lesions, in cardiology for the break up of blood clots, and in urology for the break up of urinary stones<sup>2,6</sup>. In the past ten years, the use of lasers in surgical and medical practices has increased; this market desires improved wavelength agility, low cost, and compactness of the laser system. A photostable solid-state laser could provide all of these. The output of multiple wavelengths not only allows for selective heating by preferential light absorption by the target material (e.g., oxyhemoglobin, de-oxyhemoglobin, melanin, various tattoo ink pigments), but also allows for different penetration depths of the laser light. The low cost and compactness stems from the simplicity of the laser system; solid-state dye lasers would not require

fluid pumping devices, and flashlamp pumping as opposed to laser pumping can be used, which decreases the cost and size of the laser system.

Dyes have been incorporated within a variety of solid-state hosts such as polymers, porous glasses, low temperature glasses, and sol-gel derived glasses in which low processing temperatures are used to prevent thermal degradation of the dye. Poor photostability of the dye within the host has been the major limitation of these materials. Enhancement in photostability can be achieved by optimizing the laser system design, by synthesizing a more photostable laser dye, and by controlling dye/host interactions in the gain medium. Utilizing the last method, dye/host interactions are examined for Coumarin and PM-567 dyes within sol-gel derived xerogels (air dried porous gels) and Polycerams (polymer-modified ceramic materials in which the organic and inorganic components are combined on a near-molecular scale). Polycerams are attractive hosts because they provide optically transparent, polishable monoliths, and because the physical properties of the host and dye/host interactions can be controlled through variations in processing and composition.

In this study, we will consider the mechanisms by which lasing dyes degrade, specifically for PM-567. Then a series of molecular engineering techniques, involving control of dye/host interactions which lead to improved photostability of the dye/host system, are discussed. These techniques can be used for the design and synthesis of dye/host laser materials requiring high photostability as well as other dye/host materials in which high photostabilities are desired such as those containing photochromic dyes, nonlinear optic dyes, coloring dyes, and chemical sensing dyes.

## 2. EXPERIMENTAL

**Material Synthesis.**  $\text{SiO}_2$  xerogel and  $\text{SiO}_2$ :Polydimethylsiloxane (PDMS) Polyceram hosts were doped with Coumarin and Pyrromethene dye using the sol-gel process. Details of the dye synthesis and sol-gel processing are described elsewhere<sup>7,8</sup>. As an example, one of the synthetic routes used to synthesize PM-567 doped  $\text{SiO}_2$ :PDMS Polycerams is shown schematically in Figure 1. The resulting Polycerams were optically transparent and polishable.

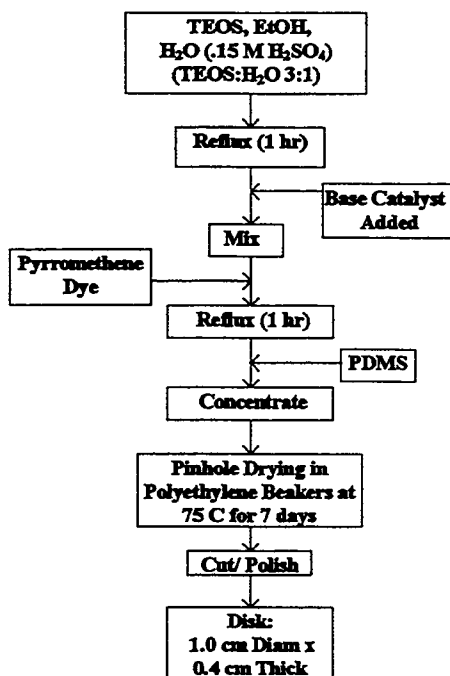


Figure 1: Synthetic Route for a PM-567  $\text{SiO}_2$ :PDMS Polyceram.

**Absorption Photostability.** Samples were exposed to a long wave UV lamp ( $>300$  nm, 8 Watts) at a distance of 1.5 inches. The absorption spectra of the samples were monitored periodically with a UV-VIS spectrophotometer (Perkin-Elmer, Lambda 3B). The maximum absorption of the dye was normalized to the absorption before UV exposure and plotted as a function of UV exposure time. The permanent drop in the absorption represents the degradation of the dye.

**Fluorescence Photostability.** Photostability was also measured by monitoring the fluorescence intensity as a function of the number of pump pulses from a Q-switched, frequency doubled Nd:YAG laser (Quanta-Ray DCR-11) at 532 nm with a pulse rate of 10 Hz, a pulse width of 6 nsec, a pulse energy of 28 mJ, and a spot size of 0.6 cm in diameter. The samples were pumped while placed within a 6 inch integrating sphere. The exiting light was passed through color filters and a spectrometer in order to collect only the fluorescent light from the sample. The spectrometer was adjusted to the wavelength which had the highest fluorescent intensity (near 577 nm). The intensity of the light exiting the spectrometer was monitored by a silicon detector. A schematic of the photostability setup is shown in Figure 2<sup>9</sup>.

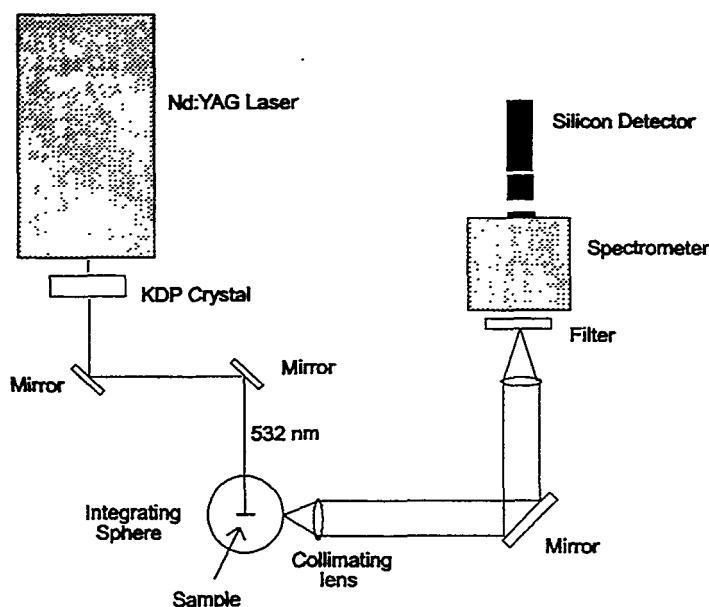


Figure 2: Schematic of the photostability measurement setup.

### 3. MECHANISM OF DEGRADATION

To improve the photostability of a particular dye/host system, one must first understand the mechanism(s) by which the dye degrades. An organic dye in its excited state can return to ground state by a number of pathways as shown in Figure 3. A number of these pathways are photochemical in nature such as dissociation, substitution, oxidation, hydrogen abstraction, and addition reactions<sup>10-12</sup>. These photochemical processes result in permanent destruction of the dye molecule. Hence in order to improve photostability, one must prevent or hinder these photochemical processes.

Review of the literature reveals that many laser dyes degrade by oxidation. This mechanism of decay was tested for the PM-567 in Polyceram monoliths. Three identical PM-567 SiO<sub>2</sub>:PDMS Polycerams (dye concentration =  $5 \times 10^{-5}$  M, sample thickness = 0.15 cm) were placed in sealed fused silica cuvettes, and an over pressure of compressed air, oxygen, or argon was passed through the cuvettes while the samples were exposed to UV light ( $>300$  nm). The absorption photostability is shown in Figure 4. The presence of oxygen caused a dramatic decrease in the photostability. In an oxygen atmosphere  $>90\%$  of the dye degraded after 74 hours; while in an argon atmosphere, only 16 % of the dye degraded in the same period. In air, the rate of photodegradation was similar to that in an oxygen atmosphere. These results suggest that oxygen plays a role in the degradation of the dye.

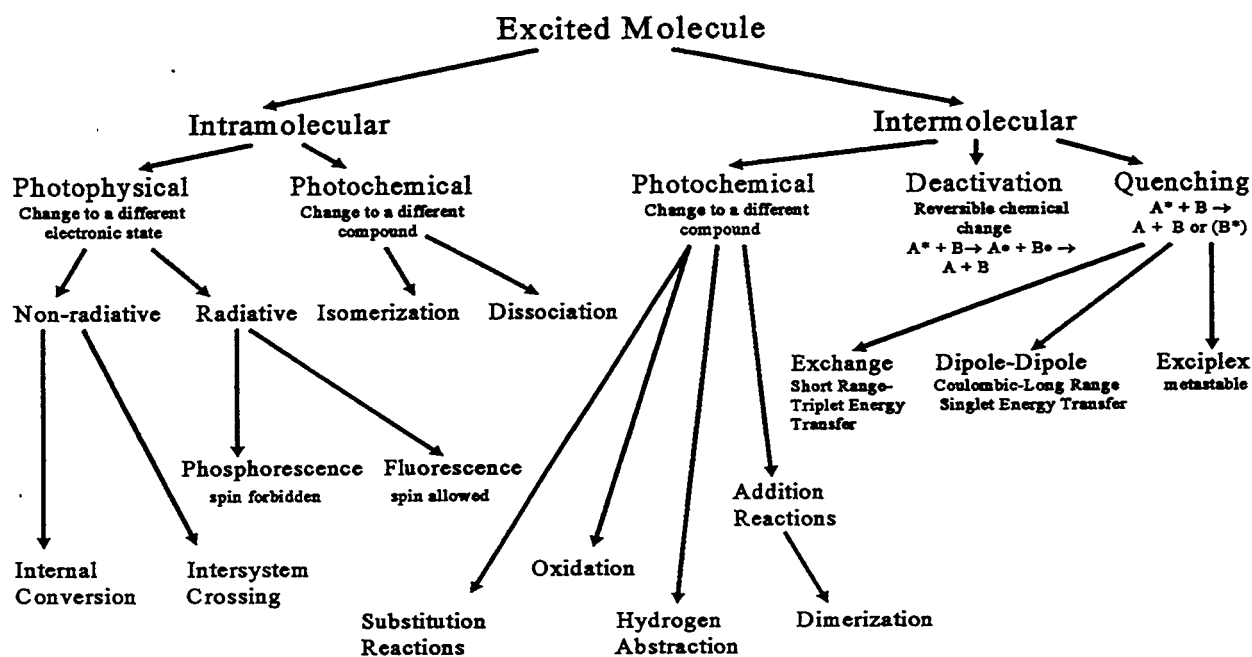


Figure 3: Decay pathways for an excited dye molecule.

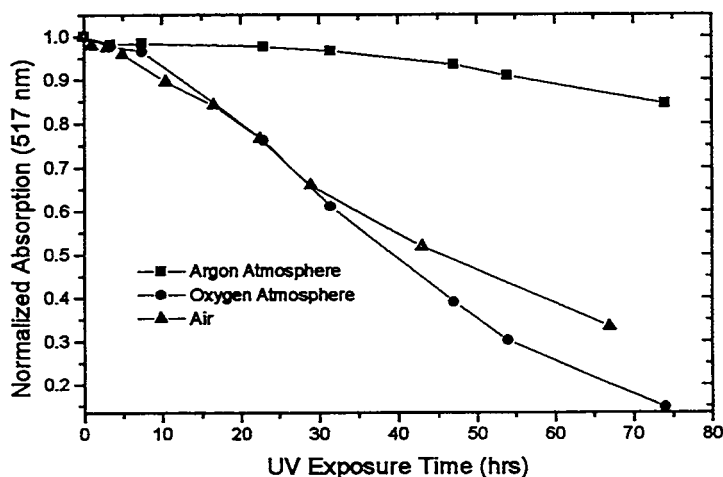
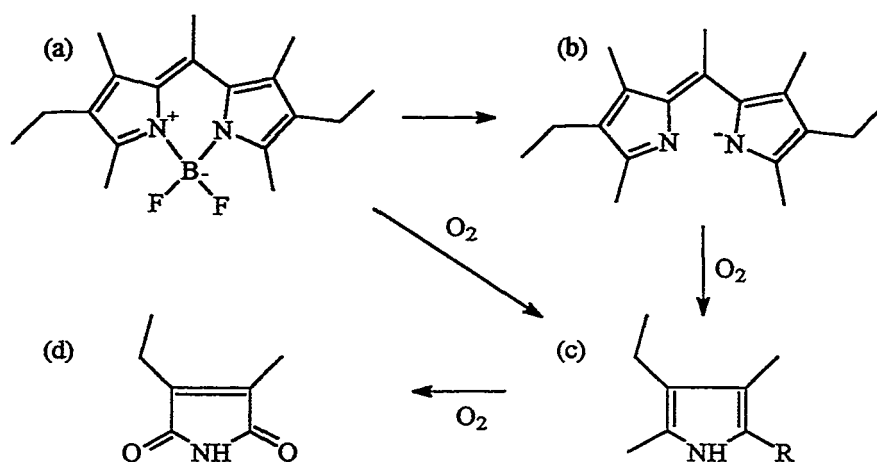


Figure 4: Absorption photostability of PM-567 doped SiO<sub>2</sub>:PDMS Polycerams in different atmospheres.

The degradation products of PM-567 were then determined by chemical analysis to confirm that oxidative products were formed. Performing chemical analysis of photo-degradation products is often difficult because the dye is dissolved in hosts at fairly low concentrations of  $10^{-3}$  to  $10^{-5}$  M, resulting in very small yields of degradation products. To maximize the yield of degradation product, a custom quartz sealed cell was designed and constructed, offering a short path length (0.3

cm), a large surface area (10 cm x 10 cm) for UV lamp excitation, and a relatively large sample volume (30 ml compared to a conventional quartz cell with 3 ml). PM-567 was dissolved in ethanol (EtOH) at a concentration of  $4 \times 10^{-3}$  M, and a high intensity UV Lamp (365 nm, 7000  $\mu\text{W}/\text{cm}^2$ ) was used to degrade the PM-567/EtOH solution for 48 hours. Before degradation, the solution was opaque red in white light; after degradation, the solution was transparent yellow. The product was isolated by evaporating the solvent. Using  $^{13}\text{C}$  NMR spectroscopy, a single major product was determined, 3-ethyl-2-methylmaleimide (-8.4 ppm, -12.6 ppm, -17.0 ppm, -137.6 ppm, -143.3 ppm, -171.96 ppm, -172.3 ppm). The presence of the C=O groups in this product (Figure 5 (d)) confirms that the degradation occurs by oxidation. Alkyl pyrroles (Figure 5 (c)) are known to oxidize to form maleimide compounds<sup>13-15</sup>. Hence it is proposed that an alkylpyrrole is an intermediate product in the degradation of the dye. The degradation products were found to vary in composition upon change in acid or basic environment, but always contained C=O substituents verifying that the dye still degraded by oxidation.



**Figure 5:** Proposed degradation route for (a) PM-567 by oxidation to (d) 3-ethyl-2-methylmaleimide.

The PM-567 dye was also found to degrade by chemical means. The chemical stability of PM-567 in the Polyceram solutions depended strongly on the catalyst(s) used to promote the sol-gel hydrolysis and condensation reactions. Reactions carried out with a highly acidic catalyst (e.g., HCl,  $\text{H}_2\text{SO}_4$ ) resulted in complete bleaching (or degradation) of the dye molecules during sol-gel synthesis. Weaker acids used as catalysts (e.g., p-toluenesulfonic acid,  $\text{HNO}_3$ ), also resulted in significant dye degradation, indicated by a large drop in dye absorptivity and a blue shift in the spectrum of the dye. Such processing conditions resulted in little or no visible fluorescence from the solutions upon UV lamp excitation (Table 1).

**Table 1:** Effect of catalyst on optical properties of the Polyceram solutions.

Catalyst used	pK <sub>a</sub>	Solution Color	Absorption Maximum (nm)	Absorption at 517 nm	Fluorescence
HCl	-7.0	colorless	none	0.00	no
p-toluene sulfonic acid	-6.0	red/ brown	498	0.50	no
$\text{HNO}_3$	-1.4	red/ orange	501	0.40	minimal
HCl /pyridine	5.25	orange	369, 516	1.90	yes
HCl / triethylamine	11.0	orange	372, 517	0.97	yes

To ensure the stability of the PM dye and to maintain the high optical quality of the sol-gel host, hydrolysis was first carried out under acidic conditions (pH=2.2), and a base (e.g., pyridine, triethylamine) was added to neutralize partially the solution (final pH=5-6) before the addition of PM-567. This procedure allowed for safe incorporation of PM-567 within the Polyceram host. The effect of different catalysts used during the chemical synthesis of the Polyceram solutions on the absorption properties are summarized in Table 1. Dye degradation is reduced or prevented by neutralization of the solution.

The pyrromethene-BF<sub>2</sub> complex bond is likely the weakest link in the structure of PM-567. During synthesis of the dye, BF<sub>3</sub> was added to 2,6-diethyl-1,3,5,7,8-pentamethylpyrromethene hydrochloride salt under basic conditions to form the pyrromethene-BF<sub>2</sub> complex. When the dye is exposed to acidic environments, the complex bond will break. Knowing that PM-567 degrades by both photo-oxidation and by acidic degradation, a possible multi-step degradation process has been proposed<sup>8</sup>: (1) acidic removal of the BF<sub>2</sub>, (2) oxidation of the C=C located between the cyclic rings, and (3) oxidation of the resulting alkylpyrroles to form maleimides (Figure 5).

Since O<sub>2</sub> plays a strong role in the degradation of the dye, it is useful to discuss the implications of the presence of O<sub>2</sub> in solvent and solid hosts. The concentration and diffusivity of O<sub>2</sub> in different hosts is summarized in Table 2. Comparing the O<sub>2</sub> concentration in air to that in solvent and PDMS, it is clear that a large amount of O<sub>2</sub> is present in the host. In fact, the dye concentration of PM-567 in a PDMS host is  $6 \times 10^{17} \text{ cm}^{-3}$  ( $5 \times 10^{-5} \text{ M}$ ), while the concentration of O<sub>2</sub> in PDMS is  $4.7 \times 10^{18} \text{ cm}^{-3}$ . The concentration of O<sub>2</sub> exceeds the dye concentration by a factor of 8. Clearly, at low dye concentrations there is more than enough O<sub>2</sub> already present in the host to oxidize all the dye.

Table 2: Solubility and diffusivity of O<sub>2</sub> in various hosts.

Host	Solubility or concentration of O <sub>2</sub>	Diffusivity of O <sub>2</sub>
Air (or pores in solid host)	$6 \times 10^{18} \text{ cm}^{-3}$	$10^{-1} \text{ cm}^2/\text{sec}$
Solvent	$1.2 \times 10^{18} \text{ cm}^{-3}$ ( $2 \times 10^{-3} \text{ M}$ ) <sup>16</sup>	$\approx 10^{-4} - 10^{-5} \text{ cm}^2/\text{sec}$
PDMS	$4.7 \times 10^{18} \text{ cm}^{-3}$ <sup>17</sup>	$1.7 \times 10^{-5} \text{ cm}^2/\text{sec}$ <sup>17-19</sup>
SiO <sub>2</sub> glass	—	$\approx 10^{-18} \text{ cm}^2/\text{sec}$ <sup>20</sup> $10^{-23} \text{ cm}^2/\text{sec}$ <sup>21</sup>

The diffusivity of O<sub>2</sub> decreases by orders of magnitude from air to solvent to PDMS (Table 4.3). However, the diffusivity of O<sub>2</sub> in PDMS compared to that in most solid polymers is very high,  $1.7 \times 10^{-5} \text{ cm}^2/\text{sec}$ . Most glassy polymers have O<sub>2</sub> diffusion coefficients around  $10^{-6} - 10^{-7} \text{ cm}^2/\text{sec}$ , while crystalline polymers have values of  $10^{-7} - 10^{-10} \text{ cm}^2/\text{sec}$ <sup>18,19</sup>. In fused silica glass, the diffusion of O<sub>2</sub> is close to zero at room temperature. Hence a dye molecule surrounded by a silica cage should be protected from O<sub>2</sub>. No data could be found for the diffusion of O<sub>2</sub> through a SiO<sub>2</sub> xerogel; but it is presumed that the O<sub>2</sub> diffusion is governed by the amount of porosity present since O<sub>2</sub> diffusion through the pores is rapid.

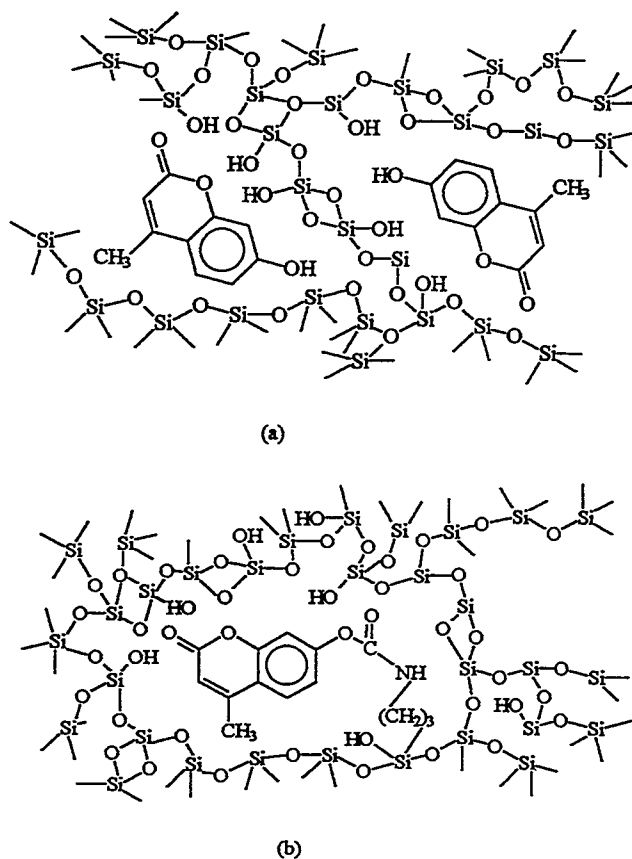
Within a SiO<sub>2</sub>:PDMS Polyceram, the diffusion of O<sub>2</sub> will depend on many factors including the polymer content and the porosity of the host. At low polymer contents, the SiO<sub>2</sub> matrix is continuous, and the O<sub>2</sub> diffusion will depend on the porosity of the sample. When interconnected porosity is present, the diffusion of O<sub>2</sub> through the bulk material should approach that in air ( $10^{-1} \text{ cm}^2/\text{sec}$ ), while with no interconnected porosity or regions of polymer, the diffusion of O<sub>2</sub> should be very low. At high polymer contents, the PDMS is continuous, and the diffusivity should be close to that of O<sub>2</sub> in PDMS. The Polyceram monoliths typically had a thickness of 0.4 cm. Using the diffusivity of O<sub>2</sub> in PDMS, the time required for O<sub>2</sub> to diffuse half way into the sample (0.2 cm) is about 40 min. Hence synthesizing the Polycerams under oxygen-free conditions would be useful, only if the material were used in oxygen-free environments or were provided with a O<sub>2</sub>-barrier coating.

## 4. MOLECULAR ENGINEERING

### 4.1 Covalently attaching Laser Dye to Host

Silylated dyes (also referred to as grafted or functionalized dyes) are dye molecules which have been chemically altered to provide alkoxysilane functionality. This allows the dye molecule itself to participate in the hydrolysis and condensation reactions during sol-gel processing. The result is a covalently bonded active molecule within a host.

Numerous silylated Coumarin dyes have been synthesized by our group with varying degrees of functionality and linkages. These dyes have been incorporated within  $\text{SiO}_2$  xerogel hosts and their optical properties (absorption and fluorescence spectra, fluorescence efficiency and photostability) have been characterized in detail elsewhere<sup>7, 22-24</sup>. The use of a silylated laser dye resulted in: (1) improved solubility of the silylated dye with respect to its unsilylated counterpart, allowing for higher concentration of active molecules within a sol-gel matrix; (2) higher fluorescence efficiency, attributed to the greater rigidity and isolation of the silylated dye within its host; (3) improved chemical stability, associated with the lack of leachability of the dye from the host; (4) control of dye/matrix interactions affecting optical spectra; and most importantly, (5) improved photostability. The improved photostability is attributed to the greater probability of trapping the silylated dye in a closed silica cage, protecting it from impurities such as  $\text{O}_2$ . The proposed structures for a conventional and a covalently bound Coumarin 4 (7-hydroxy-4-methylcoumarin) dye in a  $\text{SiO}_2$  xerogel host are shown in Figure 6, illustrating the differences in the degree of caging.

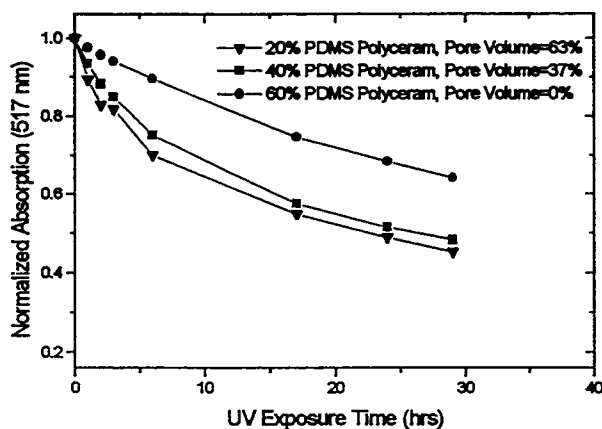


**Figure 6:** Proposed Structure of a (a) conventional Coumarin 4 laser dye (b) covalently bound Coumarin dye within a  $\text{SiO}_2$  xerogel.

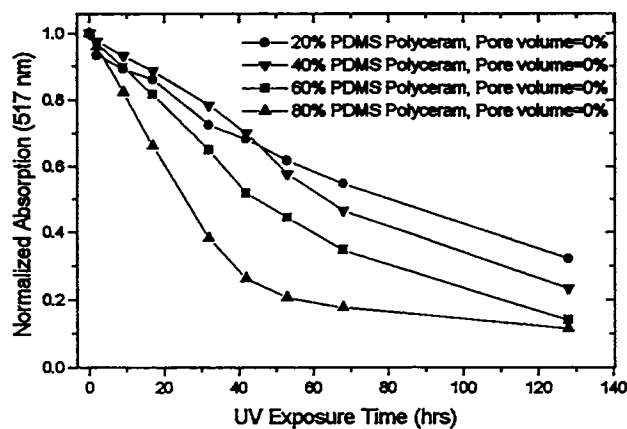
#### 4.2 Porosity and host composition

The porosity and host composition were found to affect greatly the photostability of PM-567 within Polyceram hosts. Through variations of processing conditions (water content, reflux times, drying conditions) and composition (PDMS content), it was possible to control the porosity. Details of the processing are described elsewhere<sup>8</sup>. The 20% PDMS Polyceram (a Polyceram whose composition is 20 volume % PDMS and 80 vol %  $\text{SiO}_2$ ) had a surface area of 740  $\text{m}^2/\text{gm}$  (pore volume=63%); the 40% PDMS Polyceram had a surface area of 500  $\text{m}^2/\text{gm}$  (pore volume=37%); the 60% PDMS Polyceram was essentially nonporous. The absorption photostability of these samples reveals that as the polymer content increases, the photostability improves (Figure 7a). The improvement in the photostability is attributed to the reduction in

pore volume The dye molecules which are located within the pores are more susceptible to dye degradation, since  $O_2$  has easier access to the dye molecules in the pores than to dyes located in polymer or silica cages. Also, dyes located within the pores have more rotational, vibrational, and translational modes of excitation, and are therefore more susceptible to degradation and quenching.



(a)



(b)

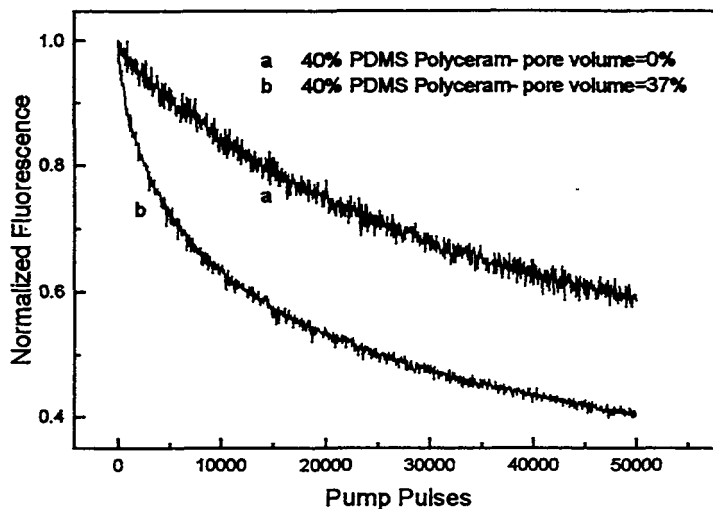
**Figure 7:** (a) Absorption photostability as function of PDMS content for PM-567 Polycerams synthesized by a route in which the porosity was a function of the PDMS content (b) Absorption photostability as function of PDMS content for PM-567 Polycerams synthesized by a route in which all compositions were nonporous.

By using another processing route (utilizing lower water content, shorter reflux times, and faster drying), it was possible to obtain nonporous samples for all PDMS contents. The absorption photostability of the nonporous Polycerams is shown in Figure 7b. The photostability improved with increasing silica content (reduction in PDMS content). Since all these samples were nonporous, it seems that a silica caging environment is required to improve further the photostability. The  $SiO_2$ -rich regions increase with decreasing PDMS content of the Polycerams.

The fluorescence photostability (shown in Figure 8) of these materials provides further evidence that porosity within the host leads reduced photostability. The nonporous Polycerame maintained more than 60% of its output after 50,000 pulses, while the fluorescence intensity of the porous sample of the same composition dropped to 60% after only 10,000 pulses. The porosity within the host tends to affect the initial drop in fluorescence more than the long term decay in the fluorescence. Several other groups have observed this initial drop in fluorescence<sup>25-28</sup>. The results in Figure 8 are likely associated with the heterogeneity of the photostabilities of the dye molecules within the host. The dye molecules are located within a variety of environments within the matrix, ranging from dyes located in open pores, to molecules in PDMS cages, to molecules in hybrid PDMS- $SiO_2$  cages, to molecules in  $SiO_2$  cages<sup>8</sup>. Dye molecules located in the open pores of the host degrade first, and dye molecules located in  $SiO_2$  cages take much longer to degrade.

The photostability of a sample depends not only on the laser dye and the host composition and structure, but also on factors such as the dye concentration, pump wavelength, pulse rate<sup>29,30</sup>, pump fluence<sup>31</sup>, sample thickness<sup>29</sup>, and geometry. With all these parameters, it is difficult to compare photostability measurements performed by different research groups. Several groups have used a parameter in GJ/mole representing the accumulated pump energy absorbed by the system per mole of dye molecules before the output pulse energy drops to half its initial value<sup>32</sup>. For the pump conditions explored here, the normalized photostability is 276 GJ/mole for the nonporous Polycerame and 87 GJ/mole for the porous Polycerame.





**Figure 8:** Effect of sample porosity on the fluorescence photostability of PM-567 in SiO<sub>2</sub>-PDMS Polycerams containing 40% PDMS.

### 4.3 Additives to improve photostability

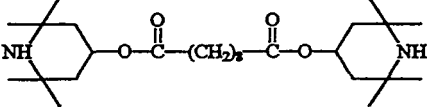
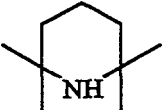

Additives to the host composition can be used to prevent photo-oxidation of the dye and to provide a more stable chemical (acid/base) environment, resulting in improved photo/chemical stability. Antioxidants are molecular species which interfere with the oxidation process by a variety of mechanisms. There are many types of antioxidants, and choosing the proper antioxidant depends on the host composition, the application, the solubility of the antioxidant in the host, the volatility of the antioxidant, and the mechanism of oxidation. Most antioxidants are used in the food industry and for polymer stabilization. In this study, antioxidants are used for dye stabilization. Antioxidants can be divided into five major classes, listed below with their effect on dye stability<sup>33</sup>:

- 1) **Absorber:** A molecule which preferentially absorbs photons which would normally be absorbed by the dye.
- 2) **Deactivator:** A molecule or metal complex which quenches the dye in its excited state.
- 3) **Interceptor:** A molecule which slows oxidation by preferentially reacting with O<sub>2</sub> or by quenching excited state O<sub>2</sub> (singlet O<sub>2</sub>).
- 4) **Free radical scavenger (Primary antioxidant):** A molecule which preferentially reacts with free radicals such as alkyl radicals (R<sup>•</sup>) and peroxy radicals (R-O-O<sup>•</sup>).
- 5) **Decomposer (Secondary antioxidant):** A molecule which reacts with hydroperoxides to prevent the formation of free radicals which accelerate dye degradation.

For laser dyes, absorbers and deactivators are not good choices since they will affect the ability of the dye to fluoresce. Hence interceptors and free radical scavengers are utilized in the present study.

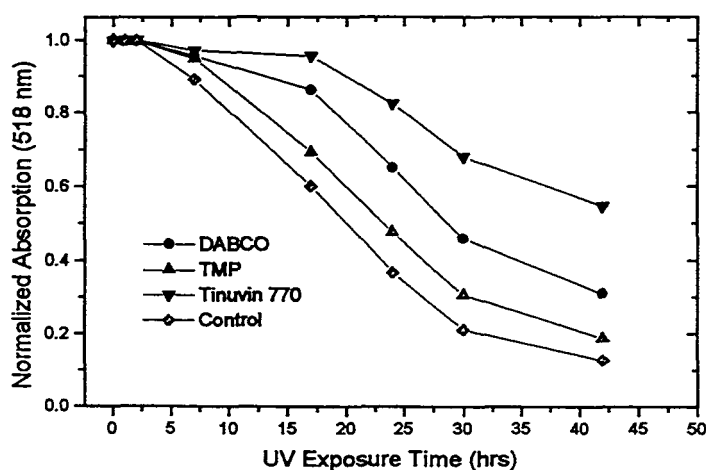
Three additives were chosen. The first two are free radical scavengers, Tinuvin 770 and 2,2,6,6-tetramethylpiperidine (TMP), which are also known as hindered amine light stabilizers (HALS). The hindered amine groups (>NH) in these antioxidants are oxidized to form nitroxyl radicals (>NO<sup>•</sup>) which preferentially react with free radicals of the dye molecule<sup>34-36</sup>. This prevents the dye radicals from initiating further reactions. The third additive, 1,4-diazobicyclo[2.2.2]octane (DABCO), is a known singlet O<sub>2</sub> quencher and has been used in the past for improving the photostability of laser dyes<sup>37, 38</sup>. DABCO is an interceptor, which works by quenching singlet O<sub>2</sub> thus preventing excited-state O<sub>2</sub> from reacting with the dye molecules. The structure and properties of the additives discussed above are shown in Table 3.

**Table 3: Properties of antioxidant and base additives.**

Additive	Type	Structure	Properties
(Tinuvin 770) bis(2,2,6,6-tetramethyl-4-piperidiny)l sebacate	HALS		mw 481 mp 83 C
(TMP) 2,2,6,6-tetramethylpiperidine	HALS		mw 141.26 bp 152C fp 24C
(DABCO) 1,4-diazobicyclo[2.2.2]octane or triethylene diamine	Singlet oxygen quencher		mw 112.18 mp 159C fp 94C pKa 8.8

mw= molecular weight, mp= melting point, fp= flash point

The absorption photostability of PM-567 in EtOH at  $10^{-5}$  M plus 1 wt % of each additive are shown in Figure 9. All the additives showed improved photostability with respect to the control (PM-567 in EtOH with no additive); the largest improvement was observed with the Tinuvin 770 additive. Since all the additives here are bases, the improvement in photostability could be attributed solely to the basic characteristic of the additive. However, this is not likely since the addition of DABCO, a strong base (pKa=8.8), resulted in a lower photostability than the addition of Tinuvin 770, a weaker secondary amine base (pKa=10.8-11.0). The results of this study suggest that antioxidant additives can be effective in improving the photostability of dye/host systems. Work is currently in progress in our group to incorporate these additives within dye doped Polyceram hosts.



**Figure 9: Absorption photostability of PM-567 in EtOH at  $10^{-5}$  M with various additives at 1 wt %.**

## CONCLUSIONS

Molecular engineering techniques to control the dye/host interactions have been proven to be effective for improving the photostability of laser dyes within sol-gel derived hosts. The degradation of PM-567 was determined to occur by photo-oxidation and by acid environments. Improved photostability was observed under the following conditions: when irradiation was carried out in an oxygen-free atmosphere; when the dye was covalently bound to the host; when porosity was removed from host; when the dye was highly caged within the SiO<sub>2</sub> environment; when the dye was placed in a chemically compatible environment; and when certain additives were added to the hosts. These molecular engineering techniques can be used for designing and synthesizing highly photostable dye/host systems.

## ACKNOWLEDGEMENTS

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